KME

2015-07-03

Extracted and translated from the project application approved by the Swedish Energy Agency

KME-717 Project Description

Title

Boiler corrosion at lower temperatures – influence of lead, zinc and chlorides

Applying organisation

Swerea KIMAB AB

Project leader

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Co-applicants

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Project

This is a new project.

Summary

Extensive work has been done on high temperature corrosion (> 450°C) caused by KCl and NaCl present in wood fuels. Much less is known about corrosion at low and intermediate temperature, 150-420°C, and particularly by Pb and Zn (and their chlorides) found in used (recycled) wood. Laboratory testing of low alloyed steel has shown that ZnCl2 is more corrosive than KCl at 250-400°C. Results from calculations have shown that the addition of sulphur to a fuel such as used wood could result in a sharp increase in $ZnCl_2$ and $PbCl_2$ in the gas phase. This project includes laboratory testing, thermodynamic equilibrium modelling, and probe testing at 150-420°C in a real boiler firing used wood with and without use of additive. The full-scale testing will give new valuable knowledge about the importance of Pb and Zn for corrosion when firing used wood and waste fuels. From this and the results of the modelling and laboratory testing solutions for minimizing potential problems will be suggested.

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Motivation

Programme relevance

The project will contribute to the following overall programme goals: Increased power production through greater electrical efficiency, improved availability and streamlined production of power and heat from renewable fuels and waste in thermal energy conversion processes; Improved fuel flexibility thanks to greater opportunities to use waste fuels which are technically complicated in terms of combustion while maintaining electrical efficiency in steam turbine processes. The project will do this by contributing to the specific technical goals number 1, 3, 5 and 6 of the programme description: examine opportunities and obstacles to achieve greater steam data; exposures of various materials to bring about greater fuel flexibility; measures to reduce boiler corrosion; suggestions for new design solutions and operating parameters to achieve enhanced fuel flexibility and availability.

The project will contribute to the programme's academic goals by having one Ph.D. student working in the project and by the results being publishing in at least one scientific peer-reviewed article. It has a direct connection to the environment quality goal “Decreased climate impact” through lowering of CO_2 emission.

Energy relevance

Serious corrosion problems are often an obstacle against utilizing used wood or waste as fuel because of its high content of chlorine and heavy metals. This issue also results in the plants having to operate at lower steam data causing decreased electrical efficiency and power production. Superheater corrosion can be mitigated allowing higher steam temperature and electrical efficiency by the use of additives, e.g. sulphur, which decreases the amount of alkali chlorides in the flue gas.

One concern is that this causes higher amount of lead and zinc chlorides in the flue gas and that this in its turn may cause corrosion. This project will help evaluating the actual risk as well as identifying countermeasures allowing safe use of higher steam temperature when utilizing used wood and possibly refuse derived fuels. This will increase the amount of electric power produced from renewables.

Industrial relevance

Boiler manufacturers will be able to construct plants operating on used wood with higher electrical efficiency through the gained knowledge on how to control the corrosion problems. The power producers will increase the amount of used wood in the feedstock lowering their production costs. Both factors will contribute to less CO_2 emission from electricity production.

News value with the project

Limited research has been made on corrosion by lead and zinc chlorides in the intermediate temperature range for CHP plants operating on used wood. Very limited research exists related to the influence of sulphur additives on this. It is expected that the project will clarify if this corrosion type is a limiting factor for the electrical efficiency that otherwise could be achieved economically through the use of sulphur additives. It is also expected that countermeasures shall be identified and be proposed to solve or mitigate the problem.

Implementation of results

Expected results are information on how to decrease the corrosion caused by lead and zinc chlorides. The results can be implemented by boiler producers to achieved increased fuel flexibility or increased electrical efficiency in new plants. It can be used by power producers to increase fuel flexibility and to decrease operational costs for existing boilers, and in some cases to increase the electrical efficiency. Further, it will help increase the boiler availability through minimised downtime caused by corrosion. The results are generally applicable to all boilers operating on used wood or mixtures of it with biomass. The information is valuable also for boilers operating on municipal or domestic waste.

Implementation of the project

The project group consists of a mixture of academic and industry partners whom are leading within the areas corrosion in boilers, boiler design, combined heat and power production and combustion chemistry. The capability of carrying out the project is excellent and there is a track record of earlier successful KME-projects. The project will be run in close collaboration between industry and academia, where the companies carry out field tests and simulations and academia laboratory testing and analysis of all samples. The results will be jointly evaluated.

Background

Combustion of biomass reduces the dependence on non-renewable energy sources, and thus the CO_2 emissions. In recent years, used (recycled) wood has become a fuel of interest due to low price compared to virgin wood-based fuels. However, used wood is often contaminated with paint, plastic and metal components, leading to elevated concentrations of heavy metals, such as zinc and lead, chlorine, sodium and sometimes sulphur in flue gases and deposits relative to those from virgin wood. In several cases, boilers burning used wood have experienced increased fouling and corrosion of furnace walls, superheaters and economisers, problems attributed to the content of chlorine, zinc, lead and alkali metals in the deposits. To minimize corrosion problems, the steam temperature is currently kept at a relatively low level and that limits electric power production efficiency.

Much work has been conducted on high temperature corrosion (> 450°C) caused by KCl and NaCl which are present in wood fuels. By contrast, much less is known about corrosion in the range 150-420°C and corrosion caused by Pb and Zn and their chlorides, which are found in used wood. Results from laboratory testing showed that $ZnCl_2$ is more corrosive than KCl in the temperature region 250-400°C on the low alloy superheater steel 10CrMo9-10 [1]. Laboratory tests also indicate that mixtures of salts, such as lead, zinc and alkali chlorides are more corrosive than what the salts are separately [2].

One way to reduce superheater corrosion caused by alkali chlorides is to use a sulphur containing additive that reacts with the alkali chlorides and forms alkali sulphates and gaseous HCl. However, results from calculations performed in KME 512 showed that the addition of sulphur to a fuel such as used wood could result in a sharp increase in $ZnCl_2$ and $PbCl_2$ in the gas phase under certain oxidising conditions [3]. It is thought that these components could cause corrosion problems at lower temperatures than what is the case with alkali chlorides.

Very limited amount of field testing, if any, has been made to investigate corrosion by lead and zinc chlorides in the intermediate temperature range for CHP plants operating on used wood and how it is influenced by sulphur additives.

As the field is almost unexplored one obstacle is to set the test parameters to investigate the most challenging situation. Through probe testing spanning the approximate temperature range 150-420°C in a real boiler firing used wood, with and without the use of additive, necessary input will be achieved to set the target for laboratory testing in the right direction. This will further be supported by modelling performed as thermodynamic equilibrium calculations.

[1] Sonja Enestam, Ph.D Thesis 2011. Åbo Akademi Report 11-04.
[2] Dorota Bankiewicz, Ph.D. Thesis2012, Åbo Akademi
[3] Figure 12. KME 512 Final report (2014)

Goal

The overarching aim of this project is to increase the efficiency of boilers firing used wood and increase the fuel flexibility of boilers. The project will examine opportunities and obstacles to achieve greater steam data; perform exposures of materials to bring about greater fuel flexibility; suggest measures to reduce boiler corrosion; and propose suggestions for new design solutions and operating parameters to achieve enhanced fuel flexibility and availability.

A specific goal of the project is to find out if lead, zinc and their chlorides causes serious corrosion problems in the temperature range 150- 420°C in boilers firing used wood, and if the attack is worsened by the use of additive that reduce alkali chloride corrosion on superheaters at higher temperatures. Based on the knowledge acquired by full-scale probe testing and the results of modelling and laboratory testing solutions for minimizing potential problems will be suggested.

Further it is a scientific goal to investigate and describe the ongoing corrosion processes and make an attempt to explain the mechanisms behind them to some extent. The results will be published in at least one scientific peer-reviewed article and is intended to be presented at an international conference as well. One Licentiate degree will be achieved during the programme period followed by a Ph.D. degree shortly after.

Project plan

Project partners: ANDRITZ Energy & Environment GmbH, AB Fortum Värme samägt med Stockholms stad, Swerea KIMAB AB, Vattenfall AB och Åbo Akademi

Field tests will be performed at one Vattenfall plant using used wood as fuel. The purpose of these tests is to evaluate the corrosive effect of lead, zinc and their chlorides and also if this corrosion is influenced by the use of additive.

Short term (3-4 hours) deposit probe testing will be performed with and without ChlorOut, a sulphur containing additive, using probes with a temperature gradient along its axis, to determine how the composition of the deposits varies with material temperature. The initial corrosion will also be examined. Long term (~1000 hours) corrosion probe testing will be performed with the use of ChlorOut, also with a temperature gradient.

Swerea KIMAB will perform analyses of the field test samples with SEM-EDS on surfaces and metallographically prepared cross-sections. Advanced techniques, such as FIB-SEM-EDS or GD-OES will be used for depth profiling of the samples. These are techniques that Swerea KIMAB has in parts further developed and successfully used during the last few years for in-depth investigation of deposits from field tests. XRD will be used to identify crystalline phases. The overall purpose is to carefully characterise the morphology and composition of the deposits and the corrosion attack, as well as correlating this to the test conditions.

Andritz will perform equilibrium calculations with Chemsheet. Andritz is using Chemsheet as Excel Add-In for thermodynamic equilibrium calculations. The basis for their calculations is a tailor-made database from Åbo Akademi (contacts: Daniel Lindberg, Mikko Hupa). This database includes beside alkalis and earth alkalis also heavy metals e.g. Pb and Zn. Thus, it is possible to calculate and predict behaviour of salts, melts and deposits comprising of these compounds, as well as gas phase and liquid phase composition. The calculation tool is basically developed also for modelling the effect of usage of additives as ChlorOut. A sensitivity analysis on behaviour of $ZnCl_2$ in dependence of sulphur content and temperature is possible and a promising method for this project.

Andritz will also provide general expertise as boiler supplier in the project. Andritz has wide experience for different kinds of boilers and deep knowledge especially for fluidized bed boiler (BFB, CFB). Expertise on fluidization and combustion behaviour, material selection, choice of additives, boiler design, thermodynamics and material selection will be part of the contribution from Andritz.

Fortum will contribute with their expertise on operation of CHP plants and on corrosion issues related to combustion of highly corrosive fuels, primarily waste.

Åbo Akademi will perform laboratory testing investigating the corrosion behaviour of several materials under isothermal conditions exposed to salts containing $PbCl_2$ and $ZnCl_2$ at moderate temperatures (150-420°C). Further, the behaviour of deposits under a temperature gradient will be investigated. Åbo Akademi will also provide expertise knowledge on thermal equilibrium calculations. Their combination of experience within the field and adapted test methods is not available within Sweden and is likely to be world unique.

The selection of test parameters for the laboratory tests will be made jointly by all partners and it will be based on the results from the performed short term field tests and thermodynamic equilibrium calculations.

By combining the results from thermodynamic equilibrium calculations, laboratory testing and probe testing in a real boiler, new valuable knowledge will be gained concerning corrosion in the temperature range150-420°C. Based on this and by the use of the combined expert knowledge of all project partners, solutions for minimizing potential problems will be suggested.

The project results will be published in at least one scientific peer-reviewed article and is intended to be presented at an international conference as well.

A Licentiate degree is expected during 2016-2017, followed by a Ph.D. degree by the end of 2018 shortly after the programme finish. It is intended that the Ph.D-student involved at Swerea KIMAB will be Annika Talus, whom is supervised by Jan-Erik Svensson at Chalmers.

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Time schedule

The project will start 2015-07-01 and finish 2018-04-15. Detailed time planning is shown in Table 1. Tasks directly involving all partners in their execution are marked in italics. The finish of each of these constitutes a milestone. Naturally, all partners will be actively involved in the discussions related to every task.

Table 1. Detailed time planning

	2015		2016				2017				2018
	Q3	**Q4**	**Q1**	**Q2**	**Q3**	**Q4**	**Q1**	**Q2**	**Q3**	**Q4**	**Q1**
Planning, preparation *(all partners)*	*X*	*X!*									
Modelling (Andritz)	X	X									
Additional modelling, at need (Andritz)			X	X	X	X	X	X	X		
Short term field tests (Vattenfall)		X	X								
Analysis short term field tests (KIMAB)			X	X	X						
Planning lab tests *(all partners)*			*X!*								
Laboratory tests (Åbo Akademi)				X	X	X	X				
Analysis lab. tests (Åbo Akademi)					X	X	X	X			
Planning long term field test *(all partners)*						*X!*					
Long term field test (Vattenfall)						X	X				
Analysis field tests (KIMAB)							X	X	X		
Combined evaluation of all results and identifying solutions *(all partners)*									*X*	*X!*	
Reporting *(KIMAB, all partners)*										*X*	*X!*

! = milestone

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Industrial reference and financing

The project is financed by 60% by the industrial partners. The remaining part constitutes financing of the academic partners by the Swedish Energy Agency.

Costs

The total costs of the project are given in Table 2, the financing in Table 3, and the cost distribution in Table 4.

Table 2. **Project total cost (kSEK)**

	2015	**2016**	**2017**	**2018**	***Sum***
Salaries	759	1 135	1 297	540	***3 731***
Consultants	0	0	0	0	***0***
Equipment	40	80	50	0	***170***
Material	20	120	20	0	***160***
Laboratory costs	20	115	125	0	***260***
Computer costs	0	0	0	0	***0***
Travel	40	60	60	10	***170***
Other costs	0	0	0	0	***0***
Indirect costs (university OH)	0	0	0	0	***0***
Sum	***879***	***1 510***	***1 552***	***550***	***4 491***

Table 3. **Financing of project (kSEK)**

	2015	**2016**	**2017**	**2018**	***Sum***
Swedish Energy Agency	189	730	627	250	***1796***
Vattenfall (in-kind)	500	510	710	300	***2020***
Andritz (in-kind)	150	200	150	0	***500***
Fortum (in-kind)	15	20	15	0	***50***
Fortum (cash to Swerea KIMAB through Energiforsk)	25	50	50	0	***125***
Sum	***879***	***1510***	***1552***	***550***	***4491***

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Table 4. **Cost distribution (kSEK)**

Part	**Year**	**Salaries**	**Consultants**	**Equipment**	**Material (incl.gases)**	**Laboratory**	**Computer**	**Travel**	**Others**	**(Indirect)**	***Sum***
Vattenfall	**2015**	400		40	20	20		20			***500***
	2016	320		80	20	50		40			***510***
	2017	540		50	20	60		40			***710***
	2018	290						10			***300***
	Sum	***1550***	***0***	***170***	***60***	***130***	***0***	***110***	***0***	***0***	***2020***
Andritz	**2015**	140						10			***150***
	2016	190						10			***200***
	2017	140						10			***150***
	2018	0									***0***
	Sum	***470***	***0***	***0***	***0***	***0***	***0***	***30***	***0***	***0***	***500***
Fortum	**2015**	15									***15***
	2016	20									***20***
	2017	15									***15***
	2018	0									***0***
	Sum	***50***	***0***	***0***	***0***	***0***	***0***	***0***	***0***	***0***	***50***
Åbo Akademi	**2015**	40						10			***50***
	2016	215			100	25		10			***350***
	2017	215				25		10			***250***
	2018	50									***50***
	Sum	***520***	***0***	***0***	***100***	***50***	***0***	***30***	***0***	***0***	***700***
Swerea KIMAB	**2015**	164									***164***
	2016	390				40					***430***
	2017	387				40					***427***
	2018	200									***200***
	Sum	***1141***	***0***	***0***	***0***	***80***	***0***	***0***	***0***	***0***	***1221***

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Extracted and translated from clarifying notes
sent to the programme council before approval

Clarifying notes

1) The field exposures are intended to be performed in the boiler Jordbro P7.

2) The project will interact closely with project KME-708. Personal from Swerea KIMAB and Vattenfall will be active in both projects and are key individuals in both projects. Among these can be mentioned in particular the Ph.D. student Annika Talus, whom will use results from both projects for her Ph.D. thesis, and whom, when applicable, will study the scientific similarities and dissimilarities that exist between these. The projects deal with similar questions and temperature ranges. An important difference is that KME-708 relates to the furnace with its low oxygen partial pressure, while KME-717 relates to the flue gas path with excess of oxygen. The influence for the corrosion mechanisms of this and other differences will be investigated in the project.

3) Condensation of sulphuric acid is known to give serious corrosion damage and exist at temperature interval up to 170 °C. This project intends to study the influence of lead, zinc and their chlorides in the temperature range 150-420 °C. Hence there is an overlap in temperature range. Nevertheless, the project will not study corrosion from sulphuric acid condensates. It is not considered industrially relevant as the condensation temperature is in principle always lower than 150 °C for plants where high levels of lead and zinc are expected, i.e. plants fuelled by used wood or waste. Sulphuric acid condensation is considered not to occur during the planned field studies. Consequently the laboratory exposures will be planned so that it is expected not to occur during these either.

   Acid dew point in the interval 150-170 °C is primarily a question when firing sour (high sulphurous) natural gas [1]. Theoretic dew points can be calculated from SO_3 levels [2], and to reach a dew point of 150 °C it is required an exceptional SO_2 level of 5000 mg/Nm^3, assuming a relevant conversion factor of SO_2 to SO_3 of 1%. Swerea KIMAB has long experience in measuring acid dew point in boilers fuelled by used wood or waste [3-6], and for these it is typical that the dew point does not exceed 110 °C. Within the project KME-413 [4] corrosion from acid condensation was measured at the plant Idbäcken, as a function of temperature. At temperatures above 100 °C the metal loss was negligible for low alloyed steel, since acid condensation was no longer occurring.

[1] Alvarez H., Energiteknik del 1, Studentlitteratur, Lund, Sweden, 1990.
[2] ZareNezhad B., Oil & Gas Journal, Vol. 107 (35), 2009.
[3] Linder M. et al., report project ECSC Contract No 7210-PR/305, 2006.
[4] Hildenwall B., Nordling M., report project KME-413, 2010.
[5] Nordling M., report no. 1230, Värmeforsk, Stockholm, Sweden, 2012.
[6] Confidential industrial assignment reports.